Microscopic Observations of Leather Looseness and Its Effects on Mechanical Properties

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Abstract

Looseness is a very troublesome issue regarding the structure of leather as well as the final leather product. It is a great concern to tanners who will go to great lengths to address it by adding different chemicals. However, its fine structure and effects on the mechanical properties are not fully understood. This investigation was devoted to gaining a better understanding of looseness based on microscopic observations of its fibrous structure and its effects on mechanical properties such as tensile strength and toughness. Microscopic studies showed visible gap between the interstitial layer and the corium layer in the loose leather. Moreover, the grain showed a sheet-like structure, whereas in normal leather, the grain layer is tightly packed together and the fiber bundles seem to be much smaller than the loose leather. Mechanical property studies showed looseness leads to a decrease in toughness. However, measurements also showed there is little change in tensile strength and elongation. Moreover, viscoelasticity studies showed that loose leather has very similar stress relaxation curves as tight leather. Both leathers demonstrated a rapid decrease in stress for the first few seconds followed by a much slower decay thereafter. The loose leather, nevertheless, has a greater initial stress than the tight leather, indicating a higher stiffness than tight leather. This study has provided a better understanding of looseness, which will lead to the development of measures to correct this defect such as adding fillers to the leather.

Resumen

La soltura [de flor] es un problemático tema en términos de la estructura del cuero así como en el producto final de cuero. Es una gran preocupación de los curtidores quienes van a extremos para evitarla por la adición de diferentes productos químicos. Sin embargo, su estructura íntima y sus efectos sobre las propiedades mecánicas no han sido plenamente comprendidas. Esta investigación fue dirigida hacia la consecución de un mejor entendimiento de la soltura basada en observaciones microscópicas de la estructura fibrosa y sus efectos sobre las propiedades mecánicas tales como resistencia a la elongación y tenacidad. Estudios microscópicos demostraron visiblemente una separación entre la capa del coreo y la capa prosiguiente [flor] en el cuero con soltura. Más aún, la flor demostró una estructura laminar, mientras que en el cuero normal, la flor tiene una estructura intensamente compactada y los haces de las fibras se ven más finos que los en el cuero con soltura. Estudios de las propiedades mecánicas indicaron que la soltura conlleva a una merma en tenacidad. Sin embargo, mediciones también demostraron que ocurre poca merma en resistencia a la tensión y valor de la elongación. Más aún, estudios viscoelásticos demostraron que el cuero con soltura posee curvas muy similares de relajación bajo tensión como las del cuero apretado [sin soltura]. El cuero suelto, sin embargo, demostró una incrementada tensión inicial que la en el cuero apretado, indicando una incrementado agarrotamiento en comparación al cuero apretado. Este estudio ha proveído una mejor comprensión de la soltura, lo cual conducirá al desarrollo de medidas para corregir este defecto tal como la adición de rellenantes al cuero.

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INTRODUCTION

When the hide is processed into leather, the subsequent removal of non-collagen components may create empty space or voids in the structure between fibrous layers, particularly, between the grain and corium.[1] These voids or open spaces may be exacerbated or enlarged by a number of leather processing factors such as bacterial degradation in the raw stock, excessive opening up in the beamhouse, and mechanical stressing. This can produce a very loose structure that is called looseness. It is often characterized by a very bumpy appearance on the leather grain surface and it is a very undesirable defect that can significantly downgrade the leather products. Although looseness is a very common issue in a tannery, its fine structure and effects on mechanical behavior are poorly understood. Therefore, we carried out a study to compare the difference between loose and normal leather that shows a tight structure and is referred as "tight" leather in this report. Viscoelasticity of a fibrous material has a close relationship with its performance. To fully understand the effects of looseness on viscoelasticity, we also studied the stress relaxation. The leather samples were stretched to a constant strain and we observed the stress change as a function of time. This experiment is very often performed to study the viscoelasticity of fibrous materials. We previously investigated the viscoelasticity of chrome-free leather, which in many respects behaves very differently from chrome-tanned leather.[2] Observations revealed that chrome-free leather tanned with glutaraldehyde has a higher hysteresis than chrome-tanned leather. Stress relaxation experiments, on the other hand, showed chrome-free leather has a longer relaxation time, indicating it has a stiffer structure than chrome-tanned leather. We also designed a linear stress rate model to predict the time-dependence of stress relaxation; our model fits the data better than the traditional Maxwell model. Moreover, observations showed the viscoelasticity of leather was affected significantly by its fatliquor content. A decrease of loading energy in a cyclic stress-strain experiment resulted from a higher fatliquor content in leather. For this current research, again we aim to demonstrate that through viscoelasticity studies, the effects of looseness on mechanical behavior could be better understood.

EXPERIMENTAL

Materials and Procedures

We obtained typical loose and tight crust leather samples from a domestic tannery. The leather had been chrome-tanned from bovine hide, split, shaved and then retanned, colored and fatliquored with the final crust thickness about 1.2 mm. We conditioned the leather in a conditioning room at 23°C and 50 percent RH according to ASTM standard method D1610-96 for one week before physical property testing.

Mechanical Property Evaluations

We performed mechanical property measurements with an Instron tensile tester to obtain tensile strength, elongation and toughness. Tensile strength is defined as the maximum stress to fracture leather. Elongation is the percent the leather stretched until failure. Toughness (also called fracture energy) was determined by measuring the energy required to fracture the leather sample, which is the area under the stress-strain curve.[3] Five samples (1 x 10 cm) were cut parallel and perpendicular to the backbone line. The tensile tests are performed on the combination of the parallel and perpendicular directions and an average of 10 specimens per sample. The moisture content of samples was determined to be 20±1 percent moisture by a Delmhorst moisture meter (Delmhorst Instrument Co.). Properties were measured at 23°C and 50% RH with a gauge length of 50 mm. An upgraded Instron mechanical property tester, model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this investigation. The strain rate (cross-head speed) was set at 50 mm/min. Each test was conducted on five samples to obtain an average value.

Acoustic Emission (AE)

To achieve a better understanding of stress-strain behavior for a fibrous material such as leather, we simultaneously performed AE measurements and tensile stress-strain tests for the samples previously described. A small piezoelectric transducer was clipped against the leather sample. This transducer resonates at 150 kHz (Model R15, Physical Acoustics Corp., Princeton, NJ) and is 10 mm in diameter. AE signals emanating from this transducer when the Instron stretched the leather samples were processed with a Model 1220A preamplifier and an upgraded LOCAN-AT acoustic emission analyzer (Physical Acoustics Corp.). The upgraded LOCAN AT, which exceeds the 20 MByte limit of old LOCAN's, is connected to a PC base with enhanced graphing and data acquisition software (Microsoft WINDOWS compatible) with all the features and options of the SPARTAN 2000. This AE system has been used in our research center for studying the deformation and fracture mechanisms of fabrics, leather and bio-composites. Our typical test samples are dumbbell or rectangular in shape with a thickness less than 3 mm.

Environmental Scanning Electron Microscopy

The field-emission environmental scanning electron microscope ESEM is advantageous over conventional scanning electron microscopy (SEM) because a relatively high vacuum in the specimen chamber is not needed to prevent atmospheric interference with primary or secondary electrons. An ESEM may be operated with a poor vacuum (up to 10 Torr of vapor pressure, or one seventy-sixth of an atmosphere) in the specimen chamber. Therefore we used ESEM to compare the structural difference between loose and tight leather. The ESEM was operated at low vacuum (0.3 Torr) with the voltage set at 15 kV, spot size 5.0 and working distance of approximately 10mm. Leather samples were uncoated, thus preserving the original characteristics of the leather samples. Samples were cut perpendicular to the long dimension of the samples and glued onto metal tabs using Duco-cement.

RESULTS AND DISCUSSION

Microscopic Observation

The fibrous structure of leather is clearly demonstrated in Figure 1. This is a micrograph of the cross-section of loose leather (Figure 1a) and tight leather (Figure 1b). It has been reported that fiber bundles (20-200 μm) of leather are comprised of very fine element fibers (10 μm), which can further be divided into even finer fibrils (0.01-0.5 μm).[4] Samples were cut perpendicular to the longest dimension from the leather samples. As shown in Figure 1a, one can see gaps in the interstitial layer between the grain and the corium layers in the loose leather. In some areas it looks like there is no interstitial area where the grain goes directly to the corium and the grain appears separated into sheet like structures in the loose leather. In the tight leather sample (Figure 1b), the grain layer is tightly packed together and the fiber bundles seem to be much smaller than in the loose leather. In addition it appears that the fibers in the fiber bundles are well divided in the regular leather, whereas in the loose leather one cannot see the individual fibers in the fiber bundles.

Figure 2a shows a more serious case of looseness, where one can observe a large separation of the fiber bundles with greater openness in the corium layer. In severe cases of looseness, one can see a clear gap between the grain and corium such as in Figure 2b.

Figure 3 demonstrates a very severe case of looseness in the corium layer and is at a much higher magnification than Figure 2. It is very evident that the leather fibers are grouped in very distinctive layers forming well separated fibrous sheets. The cross section of the loose leather in which the grain layer is separated into sheet like structures helps explain why we see the wrinkles on the leather grain when determining the break (which is a terminology used in the leather industry for the wrinkle of leather grain) of the leather. As the leather is cupped in the hand or bent in a half pipe to measure the break, the fibrous sheets stack on top of one another forming the well defined wrinkles indicated loose leather or a leather with a bad break.

AE Studies

In our research center, we have been using acoustic emission (AE) methods for characterizing leather properties. In one of our earlier AE investigations, we studied the sounds emitted by leather when it was stretched (in a tensile test)

Loose Tight

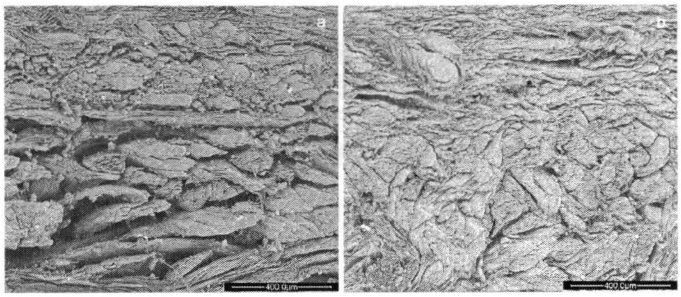

Figure 1. – Micrographs of cross-sections of (a) loose leather and (b) tight leather

Loose Leather

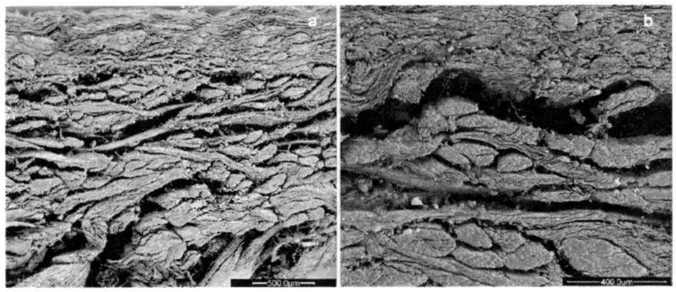

Figure 2. – Micrographs of cross-sections of loose leather

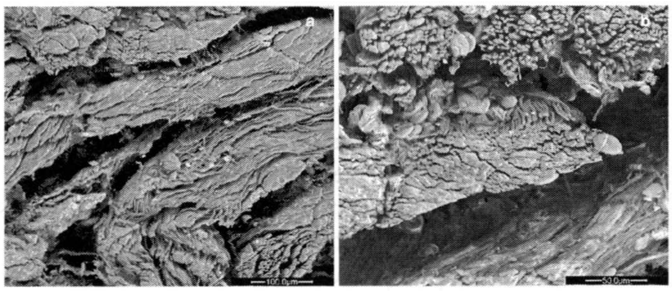

Figure 3. – Micrographs show the loose leather in which the grain layer is separated into sheet like structures

and examined the relationship between tensile strength and AE data.[5] A correlation was observed between the initial acoustic cumulative energy and the tensile strength of leather. We also designed an AE method to gain insight into the reason for tear failure.[6] In a tongue-tear test, leather samples were contacted with an acoustic sensor to collect various acoustic parameters such as AE counts, hits and energy. Measurements showed that the samples stronger in tear strength gave a significantly lower acoustic count. In contrast, the samples with poor tear strength generated more sound pulses, i.e., more acoustic counts. More recently, we established an AE method to measure the degree of opening-up of the leather structure.[7] This work was to address the urgent need for an effective means to identify the proper liming conditions that produced a sufficient degree of opening-up. We demonstrated that a history plot of acoustic emission counts could detect a change in the degree of opening up of the fiber structure associated with an increase in liming time. The results of this work have provided a route to monitor the degree of opening up of leather. Moreover, our previous studies also demonstrated that the AE technique is very instrumental in characterizing the degree of lubrication of fibrous materials treated with fatliquors.[8] The total acoustic hits from a leather sample are strongly associated with the stiffness of the leather. The stiffer the leather, the greater the amount of acoustic hits emitted in a tensile test. We also exploited the AE technique to measure the flexing endurance of leather coatings.[9] Observations showed that a change in the flexibility of the coatings can be analyzed by examining the plot of the AE count rate as a function of time. We observed that a quantitative association exists between the flexibility of coatings and the acoustic counts produced at an initial tensile stretch. The results of this AE research have provided a route to examine the flexing endurance of leather coatings. In the present study, we performed the AE tests while doing the tensile tests because we believe AE results may reveal some structural information that other methods cannot offer. Figure 4a displays the chronological course of the test, demonstrating the hits rate vs. time profiles during the tensile testing of leather. As demonstrated in Figure 4a, the loose leather sample produces twin peaks in the hits rate vs. time curve. The first peak signifies a partially fractured leather sample; with some unbroken fiber bundles still holding the leather together. The second peak shown on the figure is probably due to the subsequent breakage of those remaining fiber bundles. In contrast, the tight leather sample as shown in Figure 5a yields only one major peak. This sample emits very little sound for the first thirty-seconds stretched, followed by a steep increase in the hits rate to a peak point at around 40 seconds, and then a sudden decrease as the leather is totally fractured. Twin-peaks as shown in Figure 4a imply the existence of non-uniform stress sharing and a premature fracture in the leather structure. Therefore the first peak is ascribable to the fracture of the grain layer and the second peak is due to the corium fracture in the loose leather because of the separation of the grain and corium. In contrast, a single peak as shown in Figure 5a indicates that the tight leather structure uniformly shares the tensile stress without premature breakage or fracture as shown in the tight leather sample. Stress curves from traditional tensile tests (dotted lines) are also shown in Figure 4b and 5b, which obviously do not have the capability to reveal the difference between the loose and tight leather. The tensile test is not sensitive enough to reflect the non-even fracture that occurred in the loose leather. A fibrous structure is a necessity for the energetic acoustic activities demonstrated in Figures 4a and 5a. In other words, the acoustic hits profiles demonstrated previously are a unique phenomenon for a fibrous structure. Leather consists of collagen fibers with a very complex structure, a network of interwoven fiber bundles with large spaces unevenly distributed among them. Fiber movements produce the mechanical waves when a fibrous material such as leather is stressed. In contrast, a non-fibrous structure such as a plastic film (for example, polyester) will not be capable of emitting sound when it is stretched until it is totally fractured. For the same reason, a raw hide does not produce sound either, until the final moment of fracture.

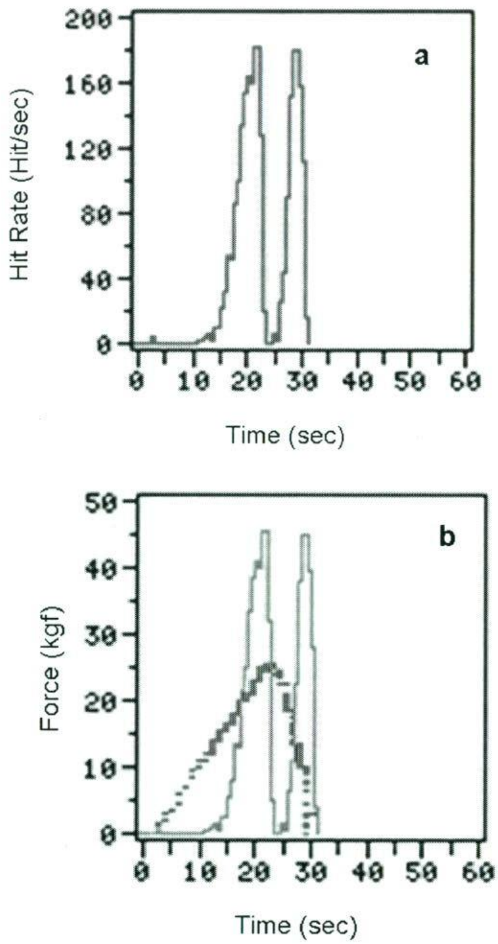

Figure 4. – (a) Hit rate vs. time; (b) force vs. time for a loose leather

Mechanical Properties

Tensile strength (1 MPa = 145 psi = 0.102 kg/mm^2) is one of the most important mechanical properties of leather. It is an indication of the maximum tensile stress a material can sustain until fracture. Elongation is another physical property closely associated with leather quality. As the name indicates, elongation refers to the ability of a material to lengthen, or stretch, when tensile stress is applied to it. It is commonly expressed as the percent increase in original length when the stress applied equals the tensile strength of the material. Therefore, elongation indicates the maximum extent to which the material can be stretched until fracture. Figure 6 shows the resultant mechanical properties of the loose and tight leather. It demonstrates very little difference between loose and tight leather in both tensile strength (Figure 6a) and elongation (Figure 6b).

Toughness has been described in a previous report as a quantity associated with the product of tensile strength and elongation.[3] Good toughness reflects a superior balance of strength and flexibility with good deformability, thereby minimizing the stress concentration and yielding a better tearing strength. We characterized the toughness of leather by measuring the energy needed to fracture a sample, which is obtained by integrating the area under the stress-strain curve. As shown in Figure 7, the tight leather has better toughness than loose leather. This is attributable to the more condensed and uniform fibrous structure in the tight leather. This leads to a more even stress sharing and results in a higher energy required to fracture leather.

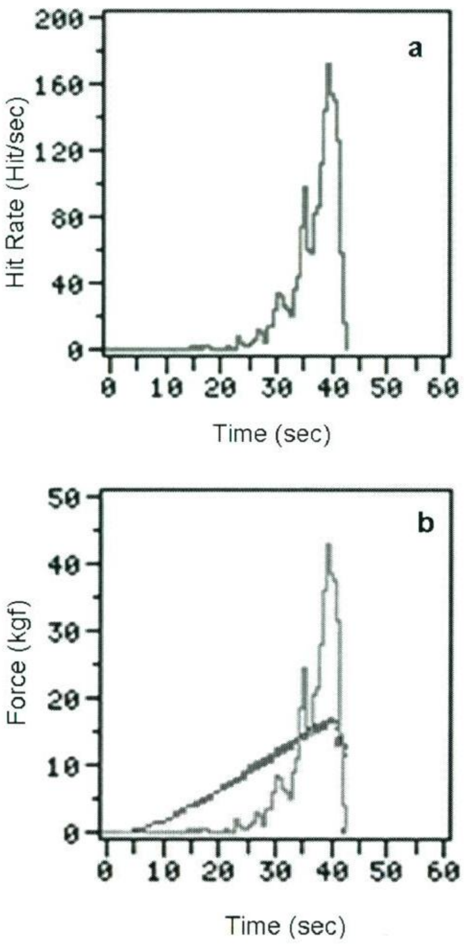

Figure 5. – (a) Hit rate vs. time; (b) force vs. time for a tight leather

Stress Relaxation

Fibrous materials such as leather generally demonstrate a mechanical behavior that may incorporate a blend of both elastic and viscous characteristics. This is referred to as viscoelastic behavior.[10-12] We previously reported that besides the elasticity, the viscous component or viscosity plays an important role in determining the stress-strain curve even at the very beginning of the leather deformation. The viscoelasticity is commonly measured by either dynamic or static tests. In the dynamic tests, a sinusoidal variation of strain is imposed to the material and a variation of the responding stress is observed. In the static tests (our current test), a constant strain or a constant stress is imposed, and the variation of the stress (relaxation) or the strain (creep) as a function of time is observed. We performed stress relaxation experiments in this study. The samples were stretched to 20% strain and then held at this constant strain for 10 minutes (600 sec). Figure 8 shows the stress as a function of time, for both loose and tight leather. It clearly shows that for all samples, the stress starts to decay as time passes. This behavior is beneficial for gaining comfort in an initial deformation as leather contacts the human body. However, if the relaxation is too much or the sample does not return to its original shape after the stress is released, then it may create bagginess.

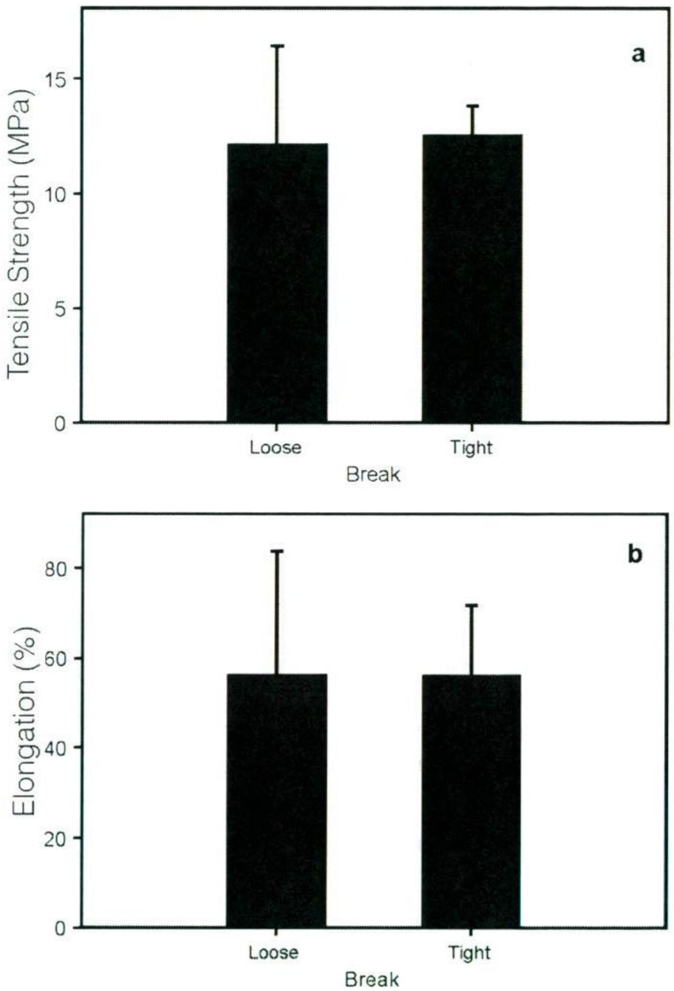

Figure 6. – (a)Tensile strength; (b) elongation

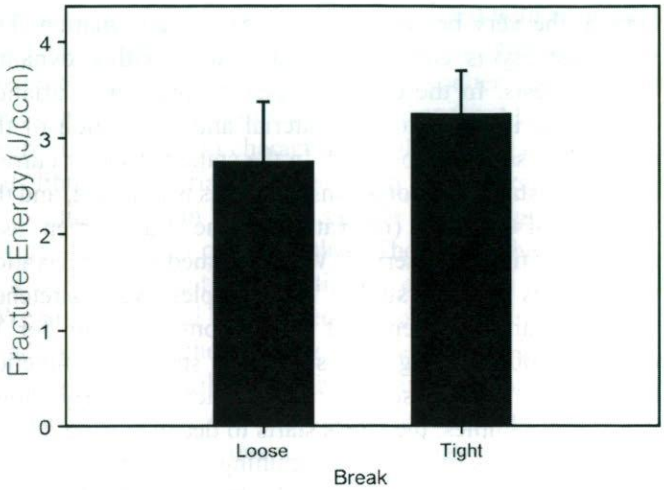

Figure 7. -. Fracture energy

The stress-relaxation behavior as shown in Fig. 8 is associated with the viscoelasticity of leather. We used a linear stress rate model to fit the stress relaxation data. One may assume that the stress rate is inversely proportional to time (t) and derive a stress equation as shown in Equation 1, where β is a constant associated with the viscoelasticity of leather. Time must be greater than or equal to 1; there is no solution for Equation 1 when t = 0; however, we observed that the difference between σ_0 and σ_1 is negligible as shown in our experiments. Consequently the solution of Equation 8 can be obtained as follows:

$$\sigma(t) = \sigma_1 - \beta \ln(t) \qquad (t \geq 1) \qquad (1)$$

The relaxation data fit this model rather well, as shown in Fig. 8. It is worth to note that there is a fast decay in stress in the first minute. This behavior actually helps in the period to break in shoes or gloves and provide a better comfort and fit for the leather products. Hereafter, the stress relaxation significantly slows down and becomes flat, thereby preventing the baggy feeling. The tight leather samples as can be seen in Figure 8 have lower stress-relaxation curves compared to the loose leather. The σ_1 value in Equation 1 is related to the stiffness of a material and therefore if we compare relaxation curves the tight leather has a lower $\sigma_1$value. On the other hand, β is associated with the stability of the leather and indicates that the tight leather sample, which has a lower β value, is more stable and softer than the loose sample.

Conclusions

Looseness is a very troublesome issue regarding leather products and tanners go to great lengths to prevent loose leather from occurring in the tanning process. This investigation has gained a better understanding of the looseness effects on the fibrous structure and mechanical properties of concern to the leather industry, such as tensile strength, elongation, and toughness. Our observations showed that a separation gap exists between the interstitial layer and the corium layer in the loose leather. Also, the grain appeared to be separated into sheet like structures. In contrast, in the tight leather, the grain layer is tightly packed together and the fiber bundles seem to be much smaller than the loose leather. Mechanical property studies showed looseness leads to a decrease in toughness and there is little change in tensile strength and elongation. Stress relaxation experiments, on the other hand, showed loose leather has a greater initial stress than the tight leather, indicating a higher stiffness than tight leather. The results from this study could lead to development of measures to correct this defect such as adding fillers to the leather.

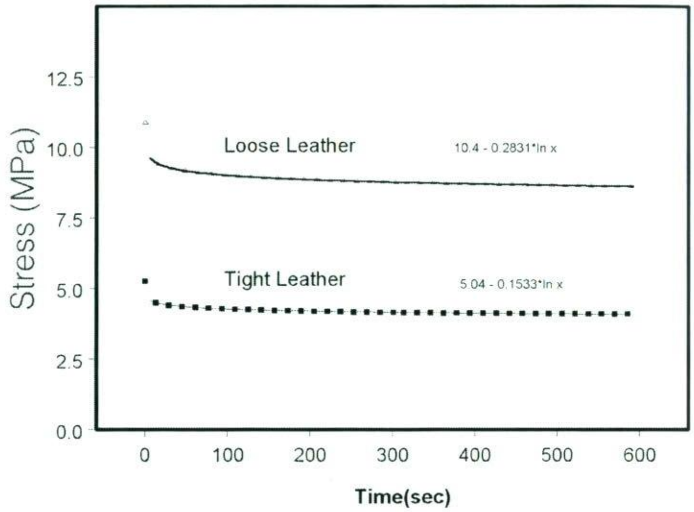

Figure 8. Stress-Relaxation curves for loose (open triangles) and tight (squares) leather.

Acknowledgments

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